



Calcium zincate as precursor of active catalysts for biodiesel production under mild conditions

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ARTICLE INFO

Article history:

Received 17 March 2009
Received in revised form 26 May 2009
Accepted 30 May 2009
Available online 10 June 2009

Keywords:

Calcium zincate
Biodiesel
Transesterification
Sunflower oil
Soybean oil
Reutilization

ABSTRACT

This work investigates the use of calcined calcium zincate as solid base catalyst for the methanolysis of sunflower oil to FAME (biodiesel). The precursor and catalyst were characterized by XRD, XPS, SEM, EGA-MS, FTIR and N₂ adsorption. The thermal treatment at temperatures as low as 400 °C leads to a base catalyst which is very active and stable in biodiesel production from different vegetable oils (sunflower and soybean). The presence of carbonate on the calcium zincate, used as precursor, is negligible after remaining in contact with air for two weeks. The catalyst obtained at 400 °C shows FAME yields higher than 90% after 45 min of reaction, and the kinetic of the heterogeneous process (60 °C, methanol:sunflower oil molar ratio of 12, 3 wt.% of catalyst) is very close to that observed under homogeneous conditions (KOH dissolved in methanol). Under these experimental conditions, the catalyst is stable against lixiviation since it can be reutilized for three catalytic runs of 1 h, reaching yields higher than 85%. Moreover, by increasing the acidity of the oil until 1.1° (typical value of fried oils), the catalytic performance is maintained. The presence of water has a negative influence on the catalytic activity, since the addition of a 0.2 wt.% of water into the reaction medium decreases the FAME yield until 80% after 3 h of reaction, although this yield is still higher than 60% after adding a 1 wt.% of water. This catalyst is also very active in the transesterification of soybean oil.

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1. Introduction

We are probably approaching the peak-high rate in consuming petroleum for energy and chemicals. Although new reservoirs may continue to emerge, the eventual ending point of natural supplies and the growing concern about environmental quality are driving an unprecedented worldwide search for alternative sources of energy and raw materials. Currently, industrial production of bioethanol and biodiesel from biorenewable resources, power generation from nuclear reactors, sunlight, or wind are also becoming increasingly efficient and affordable.

Transesterification of vegetable oils or fats for biodiesel production can be catalyzed by both acid and base catalysts [1,2]. Industrially, homogeneous base catalysts are used, including sodium or potassium hydroxides or alkoxides. Basic catalysis is preferred to the use of acid catalysis due to the corrosive character and lower activity of acid catalysts, such as sulfuric or sulfonic acids. However, removal of the base after reaction is problematic,

since the current practice of aqueous quenching with acid results in some degree of saponification (i.e., hydrolysis of the ester and formation of the corresponding sodium carboxylate), as well as the formation of emulsions which make ester separation difficult. Further, an alkaline wastewater stream is generated, which must be treated before its disposal. In order to circumvent these problems, the use of heterogeneous catalysis is of interest. In principle, this approach eliminates the need for an aqueous quench and largely eliminates the formation of metal salts, thereby simplifying downstream separation steps. Consequently, production costs should be reduced, albeit the cost of the triglyceride starting material represents the majority of the total production cost. Furthermore, the process should be rendered more environmentally friendly.

For biodiesel production, different solid catalysts have been evaluated, mainly based on alkaline and alkaline earth compounds [3–12], acid solids [13–15] and enzymes [16,17]. Moreover, the transesterification of vegetable oils can also be accomplished in supercritical methanol without catalyst [18,19]. Thus, Gryglewicz has tested the catalytic behaviour of a series of catalysts based on alkaline earth metal oxides, hydroxides and methoxides, for the methyl ester production from rapeseed oil and methanol [3],

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demonstrating that the oil transesterification can be effectively catalyzed by basic compounds derived from alkaline earth metals: calcium oxide and methoxide, and barium hydroxide. López-Granados et al. [11] have shown that CaO might be a good option like heterogeneous catalyst since this catalyst reached the maximum conversion of triglycerides within the first 60 min, with a conversion of triglycerides similar to the homogeneous catalysis. Zhu et al. [20] have also used calcium oxide, finding that the basic strength of the CaO is sufficient for the transesterification of *Jatropha curcas* oil. Nevertheless, the addition of agents to eliminate the leached calcium from the catalyst was needed to avoid its presence in biodiesel. Nanocrystalline calcium oxide showed a high catalytic activity in the conversion of soybean oil and poultry fat to biodiesel, at room temperature, but using, in the case of soybean oil, reaction times as long as 24 h [21]. Moreover, with the most active catalyst, deactivation was only observed after eight cycles when soybean oil was used. Nevertheless, an important constraint for the use of these base materials is the leaching of the active phase in the reaction medium, which would force to introduce additional stages of neutralization and elimination of these species. In addition, under these conditions, the catalytic process operating in the transesterification reaction would be mixed, with contribution of both homogenous and heterogeneous catalysis, losing the advantages of a purely heterogeneous process for the production of biodiesel. An alternative to stabilize these basic oxides against its leaching is the use of supports that facilitate their dispersion and in which the interaction support – active phase could prevent its leaching into the reaction medium. Recently, Albuquerque et al. [12] have stabilized CaO on a siliceous SBA-15 for the transesterification of sunflower oil with methanol reaching a 95% of triglycerides conversion after 5 h of reaction, without contribution of the homogenous process associated to leached calcium oxide.

On the other hand, it is known that the formation of calcium hydroxyzincate plays an important role in the retardation of cement hydration [22], as well as in slowing anode degradation in Zn/NiOOH batteries [23] and in the passivation of galvanized metal corrosion either in cement pastes or in alkaline solution. The crystal structure of calcium hydroxyzincate has been reported by Liebau and Amel-Zadeh [24]. Several authors have studied the physicochemical properties, the formation and decomposition kinetics, morphology, and cell parameters of calcium hydroxyzincate [25,26]. Due to its base character and the presence of calcium in the structure, it could be thought to be used in the transesterification of oil with methanol to yield biodiesel. Thus, the aim of our research was to investigate the use of calcium zincate hydrated as precursor to obtain basic catalysts effective in the methanolysis of sunflower oil for biodiesel production. The structural and textural characteristics of the precursor and catalyst were determined by different techniques. Furthermore, the influence of different experimental variables, such as reaction time, percentage of catalyst, presence of free fatty acids (FFA) and water in the sunflower oil, nature of the vegetable oil and reutilization, have been evaluated in order to find the most suitable conditions for biodiesel production.

2. Experimental

2.1. Catalysts preparation

Calcium zincate dihydrate was synthesized according to the procedure proposed by Ziegler and Johnson [26]. Firstly, 5 g of ZnO were dissolved in 500 mL of a 20% (w/w) KOH solution. Then, 50 g of $\text{Ca}(\text{OH})_2$, 73 mL of water and 110 g of ZnO were added to the KOH solution, under continuous stirring. The solution was aged 48 h on a rotary shaker, after that, calcium zincate dihydrate

($\text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$) was allowed to settle, and then it was filtered and washed with water until the solution pH was about 11.

The calcium zincate precursor was thermally treated *in situ* prior the catalytic tests in a tubular furnace at the desired temperature (heating rate $20^\circ\text{C min}^{-1}$), for 1 h under a helium flow.

2.2. Catalysts characterization

Powder XRD measurements were performed on a Siemens D5000 automated diffractometer, over a 2θ range with Bragg–Brentano geometry using the Cu K_α radiation and a graphite monochromator. Thermodiffactometric data were recorded on the same apparatus, which is equipped with a HTK10 heating chamber that allows heating treatments of the sample under the flow of an inert gas (ca. 25 mL min^{-1} of He). Samples were heated up to a given temperature (5°C min^{-1}). The patterns were recorded (over the angular range $10\text{--}60^\circ$, counting 1 s per step and a step size of 0.048°) after a delay time of 10 min to ensure sample thermal stabilisation.

Thermogravimetric and differential thermal analyses (TG-DTA) were performed on a Pyris-Diamond PerkinElmer apparatus. The temperature was varied from room temperature up to 1000°C , at a heating rate of $10^\circ\text{C min}^{-1}$ with a flux of atmospheric air of 100 mL min^{-1} using a mass around 15 mg.

In situ surface infrared spectra of both, calcium zincate and activated sample, were collected by diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS) using a Varian 3100 FTIR spectrometer. A Harrick Scientific Praying Mantis™ supplied with a high temperature reaction chamber mounted inside the spectrometer can provide temperature controlled flow through atmospheres attaining up to 450°C . The background spectrum was recorded with KBr purged with a 50 mL min^{-1} He flow. The DRIFTS spectra of adsorbed species were measured under a He flow in the $4000\text{--}400\text{ cm}^{-1}$ interval with a resolution of 4 cm^{-1} , collected by adding 124 scans.

The morphology of particles was studied by scanning electron microscopy (SEM) on a JEOL SM 840.

X-ray photoelectron spectroscopy (XPS) studies were performed with a Physical Electronics PHI 5700 spectrometer equipped with a hemispherical electron analyzer (model 80-365B) and a Mg K_α (1253.6 eV) X-ray source. High-resolution spectra were recorded at 45° take-off-angle by a concentric hemispherical analyzer operating in the constant pass energy mode at 29.35 eV , using a 720 mm diameter analysis area. Charge referencing was done against adventitious carbon (C 1s at 284.8 eV). The pressure in the analysis chamber was kept lower than $5 \times 10^{-6}\text{ Pa}$. PHI ACCESS ESCA-V6.0 F software package was used for data acquisition and analysis. A Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using Gauss–Lorentz curves in order to determine more accurately the binding energy of the different element core levels.

N_2 adsorption–desorption isotherm at -196°C was obtained using an ASAP 2020 model of gas adsorption analyzer from Micromeritics, Inc. Prior to N_2 adsorption, the sample were evacuated at 400°C (heating rate $10^\circ\text{C min}^{-1}$) for 1 h, in the same way of catalyst activation. Pore size distributions and pore volume were calculated with the BJH method.

Evolved gas analysis at programmed temperature by mass spectrometry (EGA-MS) was carried out. The evolved H_2O and CO_2 , arising from the decomposition of the calcium zincate, were monitored by recording the $m/z = 18$ and 44 signals, respectively. 80 mg of the sample was loaded in quartz microreactor and $50\text{ mL (STP) min}^{-1}$ of He were passed through while the sample was heated at $10^\circ\text{C min}^{-1}$. A quadrupole mass spectrometer, model BALZERS Prisma QMS 200 controlled by BALZERS

Quadstar™ 422 software, was connected on-line to the reactor outlet for the analysis of gases generated.

2.3. Catalysts activity

The methanolysis of edible sunflower oil was performed in glass batch reactor with a water-cooled condenser, controlled temperature (60 °C) and inert atmosphere (N₂). Before the reaction, the catalysts were activated at different temperatures for 1 h (heating rate, 20 °C min⁻¹) under a helium flow. Once the catalyst reached the room temperature, 15 g of oil was added, and the mixture was heated under strong stirring (1000 rpm) up to 60 °C. Then, methanol (Sigma–Aldrich, ≥99.8%, A.C.S. Reagent, H₂O < 0.1%) was added to the oil–catalyst mixture by using the dropping funnel. The methanol/oil molar ratio was 12.

Aliquots (ca. 1 mL) were taken at different reaction times and then were quenched by adding 1 mL of 0.1 M HCl aqueous solution and agitating for few minutes. Later, 1.5 mL of dichloromethane was added, and this mixture was again agitated and set aside to develop two phases: the ester phase containing dichloromethane, mono-, di- and triglycerides and FAME (and traces of methanol and glycerol) and the polar phase containing glycerol, methanol, hydrochloric acid and metal chlorides (and traces of esters). The dichloromethane was then removed from the organic phase by evaporation at 90 °C. The composition of the transesterification products derived from the methanolysis of sunflower oil was determined by high performance liquid chromatography (HPLC) using a JASCO liquid chromatograph equipped with quaternary gradient pump (PU-2089), multiwavelength detector (MD-2015), autosampler (AS-2055) and column oven (co-2065) using a PHENOMENEX LUNA C18 reversed-phase column (250 mm × 4.6 mm, 5 μm). The solvents were filtered through a 0.45 μm filter prior use and degassed with helium. A linear gradient from 100% methanol to 50% methanol + 50% 2-propanol-hexane (5:4, v/v) in 35 min was employed. Injection volumes of 15 μL and a flow-rate of 1 mL min⁻¹ were used. The column temperature was held constant at 40 °C. All samples were dissolved in 2-propanol-hexane (5:4, v/v). The weight content in FAME determined by HPLC was considered to represent the wt.% yield in FAME of the catalytic process assuming that, during the neutralization and the rinsing process of the ester phase, only traces of esters were transferred to the polar phase and that only the extraction of methanol and glycerol takes place.

3. Results and discussion

3.1. Characterization of materials

The powder X-ray diffraction pattern of the precursor confirms that a calcium zincate dihydrate, CaZn₂(OH)₆·2H₂O, has been synthesized (Fig. 1). The narrow and intense diffraction peaks can be indexed in the monoclinic crystal system, *P*2₁/*c* space group, with 2θ (°): 14.20 (1 0 0), 17.71 (0 1 1), 21.52 (1 2 0), 28.42 (2 0 0) and 36.47 (2 1 1).

The thermal transformations of calcium zincate have been studied by thermogravimetry (Fig. 2). The XRD pattern at 100 °C is identical to that of precursor. This fact is supported by the TG-DTA analysis (Fig. 3) where the weight loss starts at 120 °C. From this temperature, the calcium zincate decomposes as evidences the important weight loss in the TG curve, extending from 120 up to 300 °C and associated to two endothermic effects at 129 and 167 °C in the DTA curve. This process corresponds to the dehydration and dehydroxylation of the calcium zincate precursor. Thus, the diffractogram at 200 °C (Fig. 2) only shows peaks associated to the hexagonal ZnO (2θ (°): 31.71, 34.38, 36.23, 47.54 and 56.42) without diffraction peaks of any calcium specie. Between 300 and 600 °C, weak diffraction peaks of Ca(OH)₂ are

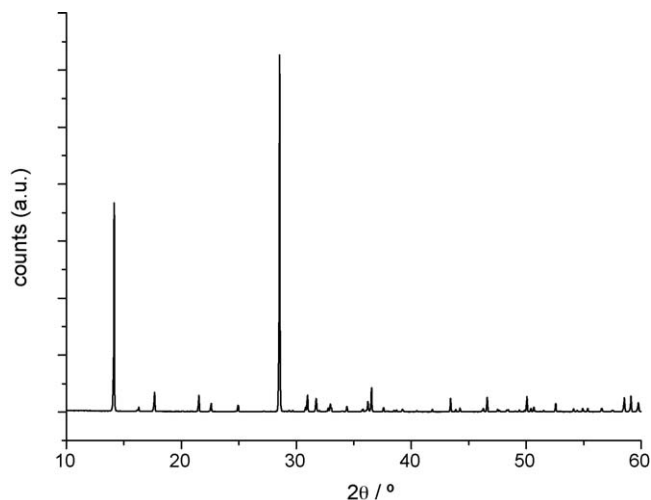


Fig. 1. Powder X-ray diffraction pattern of calcium zincate dihydrate.

visible at $2\theta = 29.26^\circ$ and 33.91° . The dehydroxylation of Ca(OH)₂ takes place in this range of temperatures (TG curve, and endothermic effect in DTA at 372 °C) provoking the transformation of Ca(OH)₂ into CaO whose diffraction peaks are clearly observed from 500 °C (2θ (°): 32.12, 37.18 and 53.56). Therefore, calcium zincate dihydrate is thermally transformed in a mixture of ZnO and CaO, but the formation of well-crystallised phases needs at least temperatures higher than 500 °C. The XRD and TG-DTA data agree well with those by Wang et al. [25].

The Ca contents have been determined by ICP-AA, and the values found of 19.9% and 25.1% CaO match well with the theoretical ones of 18.2% and 25.6%, for precursor at room temperature and after thermal treatment at 400 °C, respectively. The surface characterization of both precursor and activated materials has been carried out by XPS (Table 1), and the binding energies (BE) of CaO, Ca(OH)₂, CaCO₃ and ZnO are displayed for comparison. The presence of potassium, employed during the synthesis of the calcium zincate, was not detected neither XPS nor EDX coupled to SEM. The Zn 2p_{3/2} signals are symmetrical and, after activation at 400 °C, a shift from 1022.0 to 1021.5 eV is observed, which matches well with the presence of crystalline ZnO (1021.5 eV). The O 1s spectra of bulk ZnO presents a asymmetrical

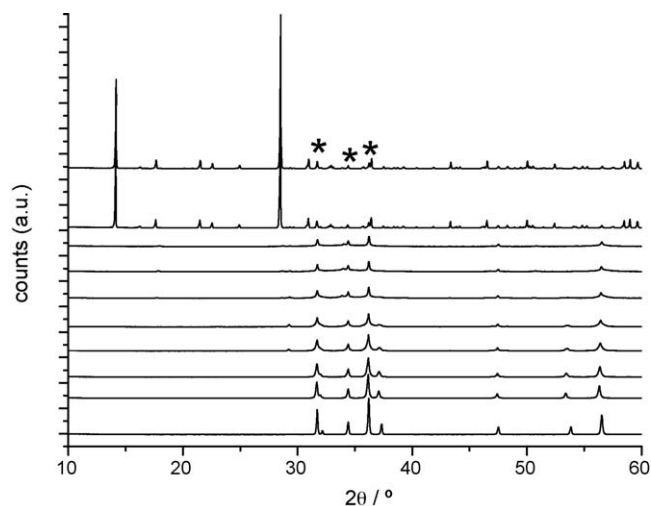
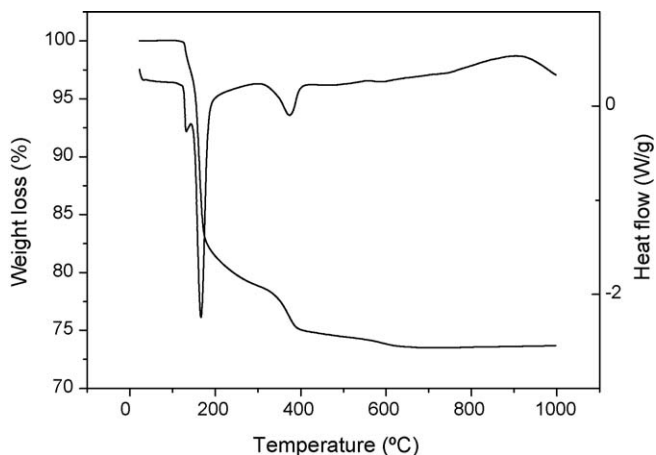


Fig. 2. Thermogravimetric study of calcium zincate hydrate: room temperature, from 100 up to 800 °C, under helium at temperature intervals of 100 °C, and stabilization at 30 °C (from top to bottom) (*: ZnO).

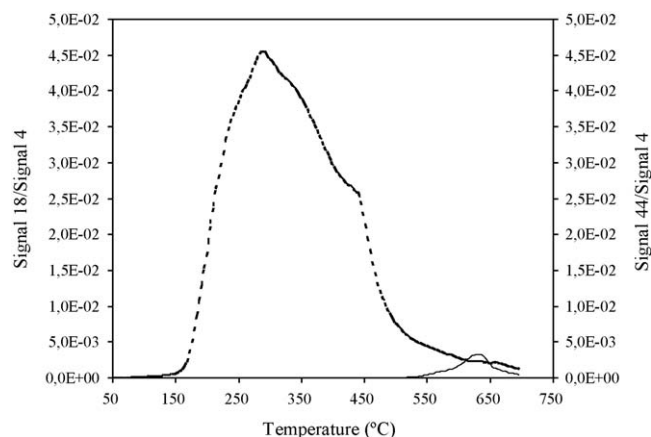
Table 1

Binding energies (eV) of Zn, O, Ca and C, as deduced by XPS (in parenthesis, the percentages of the different contributions are indicated).

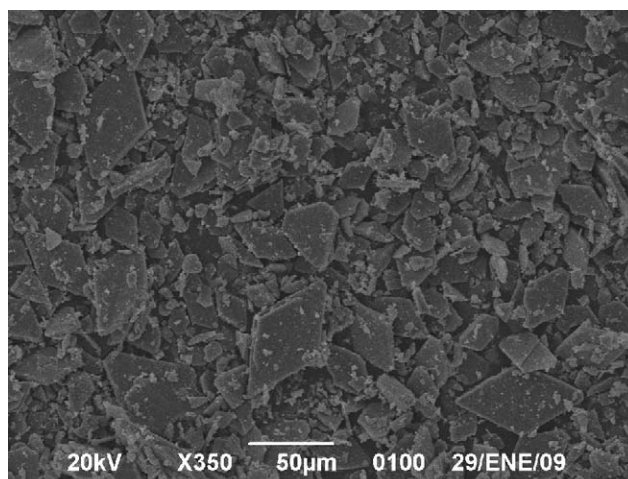
Sample	Zn 2p _{3/2}	O 1s	Ca 2p _{3/2}	C 1s
CaO [*]	–	531.3	346.9	284.9 (59), 289.6 (41)
Ca(OH) ₂ [*]	–	531.2	346.6	284.9 (61), 289.6 (39)
CaCO ₃ [*]	–	531.6	347.3	284.8 (52), 289.8 (48)
ZnO [*]	1021.4	530.0, 531.5 sh	–	284.9 (100)
CaZn ₂ (OH) ₆ ·2H ₂ O	1022.0	531.6	347.2	284.8 (85), 289.7 (15)
Activated at 400 °C	1021.5	530.0 (35), 531.6 (65)	346.7 (44), 347.6 (56)	284.8 (73), 289.8 (27)

^{*} Commercial (from Aldrich).**Fig. 3.** DTA-TG curves of calcium zincate dihydrate.

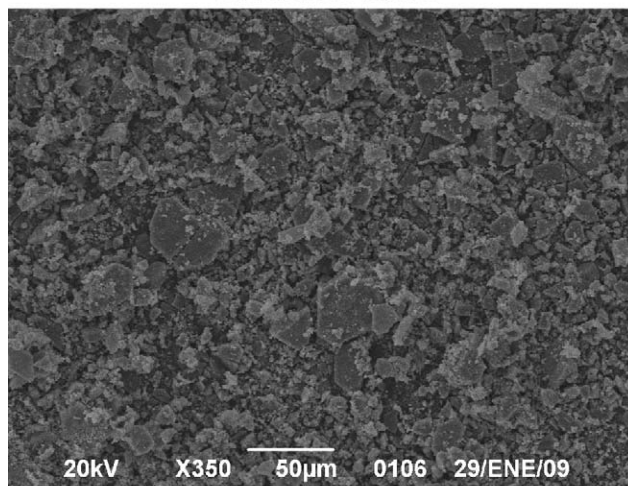
band which can be deconvoluted in two components at: (i) 530.0 eV, due to oxide ions in the crystalline network and (ii) 531.5 eV, attributed to the ionization of oxygen species compensating some deficiencies in the subsurface of ZnO [27]. The O 1s spectrum of the calcium zincate precursor is composed of a symmetrical peak at 531.5 eV corresponding to OH and H₂O groups. All studied samples show two main components in the C 1s region at ca. 284.8 and 289.8 eV, except crystalline ZnO which only has the low energy component. The C 1s BE at 284.8 eV is assigned to carbon from adventitious hydrocarbons (C–H groups) and the other high BE band to carbonate species. This is confirmed by comparing with the calcium carbonate, where the atomic CO₃²⁻/Ca ratio is close to 1. The presence of carbonate has been already detected by EGA-MS (Fig. 4), and the XPS data confirms the existence of surface carbonate species, mainly associated to calcium. The atomic Zn/Ca and O/(Ca + Zn) ratios are, respectively,

**Fig. 4.** EGA-MS study of calcium zincate dihydrate: H₂O (dashed line) and CO₂ (solid line).

2.17 and 2.42, which are not so different of the nominal values corresponding to the calcium zincate (2 and 2.7, respectively). After activation at 400 °C, the atomic Zn/Ca ratio increases until 3.89 due to the heterogeneous distribution of crystalline ZnO and calcium species. The Ca 2p_{3/2} signal can be deconvoluted into two components: 346.7 and 347.6 eV; the first one could be ascribed to CaO and the second to CaCO₃/Ca(OH)₂. The surface carbonation and hydroxylation also stem from the contact of the activated sample with air during the transfer from the activation oven to the XPS chamber. The O 1s core level band exhibits two maxima with similar intensity at 530.0 and 531.6 eV, which can be attributed to oxygen associated to zinc (ZnO) and calcium species, although ZnO also contributes to the second signal. In all cases, the spin-orbit split 2p doublet is well resolved ($\Delta \sim 3.5$ eV).



Calcium zincate dihydrate



After thermal activation at 400°C

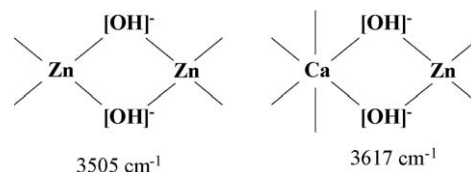
Fig. 5. SEM micrographs of the calcium zincate dihydrate and after thermal treatment at 400 °C.

The textural properties, obtained from the corresponding N_2 adsorption–desorption isotherm, are very different from those typical of pure metal oxides, since BET surface area ($76.7 \text{ m}^2 \text{ g}^{-1}$) and pore volume ($0.144 \text{ cm}^3 \text{ g}^{-1}$) values are higher than those reported for bulk CaO obtained from calcined CaCO_3 [28] and ZnO [29]. It is noteworthy that the pore size distribution is relatively narrow and centered around 4.3 nm, with a FWHM of 3 nm.

SEM image (Fig. 5) of the calcium zincate shows the existence of tetragonal crystallites, with particle sizes ranging from 5 to 90 μm , and, after activation at 400 $^\circ\text{C}$, this morphology is still observed, although the particles are smaller and with more irregular forms.

Fig. 6 displays the FTIR spectra of the calcium zincate precursor, which includes the spectra of as synthesized and after 14 days in contact with air (Fig. 6A). Moreover, it is also shown the evolution of the calcium zincate by FTIR as a function of the activation temperature under a helium flow (Fig. 6B).

Fig. 6A reveals that any new band is developed when the calcium zincate precursor is in contact with air. In the range of hydroxyl groups, it is observed three bands at 3643, 3617 and 3505 cm^{-1} . The weak band at 3643 cm^{-1} is normally ascribed to $-\text{OH}$ groups of $\text{Ca}(\text{OH})_2$ [30]; this fact could be point to the presence of terminal $\text{Ca}-\text{OH}$ groups. The bands at 3617 and 3505 cm^{-1} are due to the stretching vibration of two types of $-\text{OH}$ groups. Lin et al. analyzed the FTIR spectrum of calcium hydroxyzincate and



Scheme 1.

concluded that these bands were due to the stretching vibration of hydroxyl ions $[\text{OH}]^-$ represented in Scheme 1 [31]. In this region, the stretching mode of lattice water is also recorded. The band at ca. 1600 cm^{-1} is ascribed to the bending mode of $\text{H}-\text{O}-\text{H}$. The band at $\sim 1090 \text{ cm}^{-1}$ is attributed to the $\text{Zn}-\text{O}-\text{H}$ bending vibration [31]. In addition, a shoulder at 1433 cm^{-1} is observed, which could be assigned to the carbonate presence during the synthesis which is not carried out under inert atmosphere and therefore, some carbonation of the alkali reaction medium could take place.

The evolution the calcium zincate as a function of activation temperature has been followed by FTIR spectroscopy (Fig. 6B). This figure shows two noteworthy facts. Firstly, the bands at 3617 and 3505 cm^{-1} disappear at temperatures higher than 100 $^\circ\text{C}$ and the band at 3643 cm^{-1} shifts towards lower wavenumbers (up to 3633 cm^{-1}) being this band due to hydroxyl groups associated to calcium ions. Secondly, the band at 1090 cm^{-1} also disappears. These two facts indicate that calcium zincate suffers a structural transformation as it was shown previously by XRD. Moreover, the presence of carbonates is confirmed by the broad band centered at 1465 cm^{-1} , although the amount of carbonate is very low according to the EGA-MS results which only show a very weak band of evolved CO_2 centered at 630 $^\circ\text{C}$ (see Fig. 4). These carbonates have a superficial character since no vibration bands of bulk calcium carbonate are detected [11].

3.2. Catalytic activity

The catalytic activity of thermally activated calcium zincate has been evaluated in the transesterification of sunflower oil with methanol, under heterogeneous conditions. A stirring rate of 1000 rpm was employed in all experiments, since in a previous work by using a similar experimental procedure [12], it was found that this rate is enough to reach a suitable contact between oil, methanol and catalyst, and diffusion limitations are avoided. In addition, a methanol:oil molar ratio of 12, exceeding the stoichiometric value, and a reaction temperature of 60 $^\circ\text{C}$ were used to favour the biodiesel formation. The influence of parameters such as activation temperature, catalyst loading, reaction time, presence of free fatty acids (FFA) and water, on the catalytic performance have been evaluated.

It has been previously observed that calcium zincate decomposes at temperatures higher than 150 $^\circ\text{C}$ and the main weight loss is extended until 400 $^\circ\text{C}$. For this reason, the influence of the activation temperature of the precursor on the catalytic performance has been evaluated. It can be observed in Fig. 7 that, at 350 $^\circ\text{C}$, more than 3 h are needed to reach a FAME yield higher than 90%. This fact can be explained by taking into account that, at this temperature, $\text{Ca}(\text{OH})_2$ is still present on the catalyst surface (as shown by IR spectroscopy), and the number of strong basic sites, mainly associated to oxide species, is therefore low. By increasing the activation temperature until 400 $^\circ\text{C}$, the dehydroxylation process is completed and FAME yield higher than 85% are reached, after 2 h, and full conversion of triglycerides is observed after 3 h of reaction. Therefore, it is evident that a temperature of 400 $^\circ\text{C}$ is enough to thermally transform calcium zincate hydrate in a basic catalyst active in the methanolysis of sunflower oil. It can be supposed that the active sites for transesterification are located on

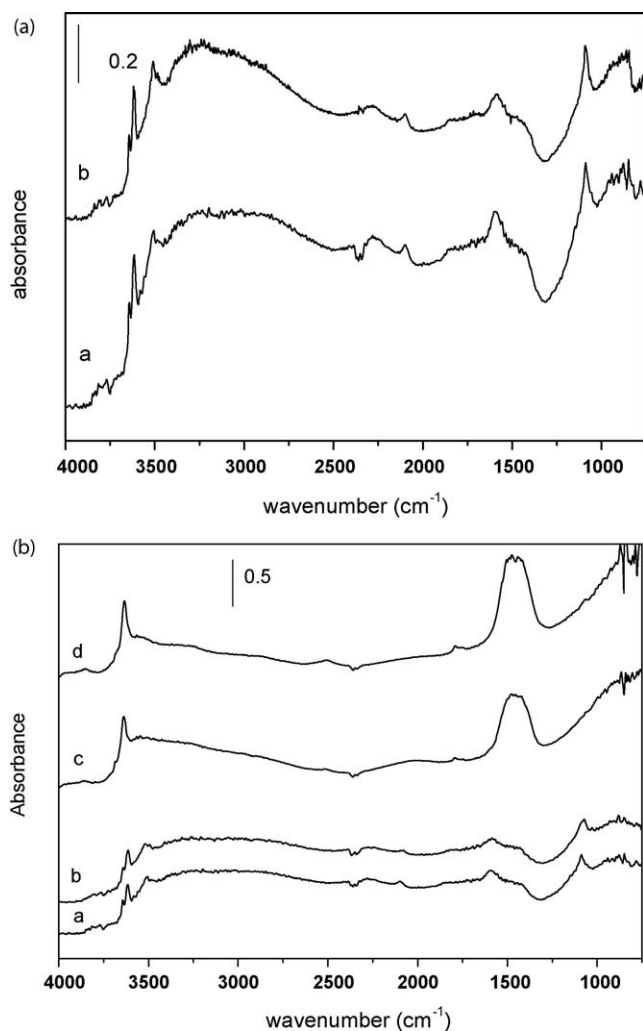


Fig. 6. (A) FTIR spectra of (a) calcium zincate dihydrate and (b) after 14 days in contact with air; (B) FTIR spectra of calcium zincate dihydrate as a function of the activation temperature under a helium flow (a) room temperature, (b) 100 $^\circ\text{C}$, (c) 300 $^\circ\text{C}$ and (d) 400 $^\circ\text{C}$.

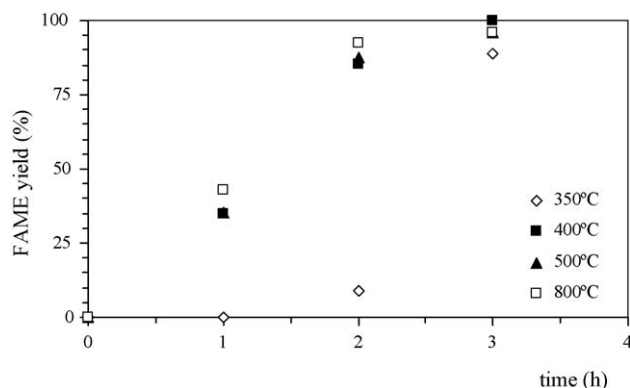


Fig. 7. FAME yield as a function of the activation temperature of calcium zincate dihydrate (1 wt.% precursor, methanol:sunflower oil molar ratio = 12, reaction temperature = 60 °C).

the oxidic surface of CaO promoted by ZnO, although the formation of surface methoxide or glyceroxide species, previously reported as active species in other papers dealing with CaO-based catalysts [28], cannot be ruled out. Nevertheless, it is noticeable that this activation temperature is 400 °C lower than the necessary to activated bulk CaO to reach a similar FAME yield [11], and 300 °C lower than that reported for Ca and Zn mixed oxides [29], to get a FAME content of 93%, but employing a 10 wt.% of catalyst, methanol:oil molar ratio of 30 and a reaction time of 3 h. This supposes an important advantage regarding the economic cost associated to the activation of solid catalysts, mainly when the elimination of carbonate species must be accomplished.

Fig. 8 illustrates the effect of the precursor loading on the FAME yield, and it can be observed that with a 4 wt.% of calcium zincate activated at 800 °C, and after 1 h of reaction, a yield of 94% can be reached, and differences are only evident at short reaction periods (1 h). It must be kept in mind that these percentages do not correspond to the actual percentage of active catalyst, since, after calcination, a weight loss close to 25% is observed in the TG analysis. Therefore, a 4 wt.% of precursor corresponds to a 3 wt.% of active catalyst.

A key aspect in the development of new solid catalysts for biodiesel production, under heterogeneous conditions, is the evaluation of the lixiviation of active species. The existence of metal ions coming from the catalyst in the biodiesel would involve stages of washing and purification of biodiesel, thus removing one of the most important advantages of a heterogeneous process against a homogeneous one. Previous studies have demonstrated

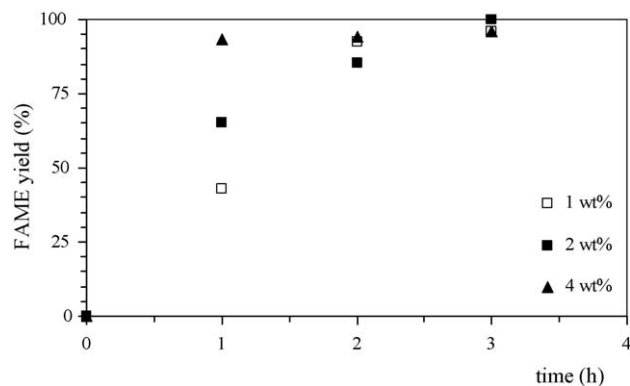


Fig. 8. Influence of the precursor percentage on the FAME yield (activation temperature = 800 °C, methanol:sunflower oil molar ratio = 12, reaction temperature = 60 °C).

that bulk CaO is partially dissolved in the methanolic solution [11,32]. The experimental procedure followed to evaluate the contribution of the lixiviated species to the overall catalytic activity consists in putting in contact the catalyst, obtained after activation of the calcium zincate at 400 °C, with methanol at 60 °C for 3 h. Then, the catalyst is removed by filtration and methanol, preventing the contact with air, is mixed with the sunflower oil and stirred for 3 h at 60 °C, using a methanol:oil molar ratio of 12. The analysis of the resulting solution revealed a FAME yield of zero, thus indicating the absence of lixiviated species with catalytic activity. This result seems to point that the calcium zincate activated at 400 °C is stable against lixiviation, unlike other studies dealing with bulk CaO where an important contribution of lixiviated calcium species was observed. Thus, under the same experimental conditions, bulk CaO and mixed CaO–SrO give rise to FAME yield of 8.5% and 23.6%, respectively. On the other hand, López-Granados et al. [11] found that a mixture of methanol–oil–homogenous species derived from activated CaO gives rise a FAME yield of 60%. Nevertheless, it can be thought that solid catalyst is lixiviated and soluble species are not active in the transesterification of triglycerides. For this reason, we have performed a reutilization study of the catalyst. Fig. 9 demonstrates that the catalyst can be reutilised during three catalytic runs of 1 h, reaching FAME yields higher than 85%. Moreover, during the recuperation of the catalyst between runs, precaution about the possible carbonation of the catalyst in contact with air has not been taken. Therefore, it can be affirmed that there is not losses of catalysts by solubilisation of active species, since in that case, a reduction in activity would be observed. The stability of calcium oxide could be attributed to its strong interaction with a much less soluble zinc oxide, which is favoured by the excellent textural properties of the resulting catalyst.

It is well known that catalysts based on calcium oxide are carbonated in contact with air, giving rise to the formation of calcium carbonate which requires very high calcination temperatures (sometimes, higher than 800 °C) to be decomposed. In order to study the stability of calcium zincate hydrate in air, we have left during 14 days a certain amount of precursor in air, and then it was activated at 400 °C and its catalytic performance was evaluated. Fig. 9 demonstrates that the precursor can be left in contact with air without needing an activation temperature higher than 400 °C, since after thermal treatment at this temperature a 4 wt.% of precursor gives rise to a FAME yield of 91%. Moreover, the transesterification of soybean oil by using this catalyst also leads to values close to 100% after 1 h (4 wt.% of precursor), thus confirming its excellent catalytic activity in biodiesel production under

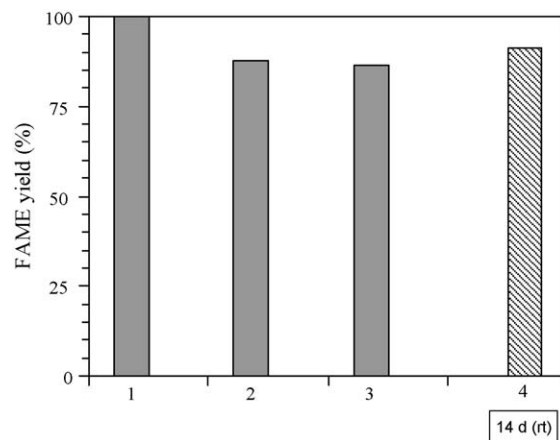


Fig. 9. Effects of the reutilization of catalyst and stability in air of the precursor on the FAME yield (4 wt.% precursor, activation temperature = 400 °C, methanol:sunflower oil molar ratio = 12, $T = 60$ °C, $t = 1$ h).

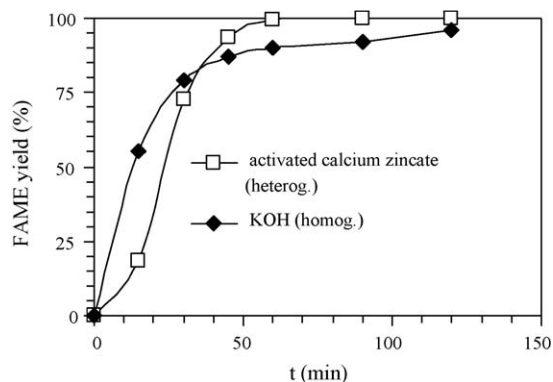


Fig. 10. Evolution of the conversion with the time for KOH dissolved in methanol (0.2 wt.% catalyst) and activated calcium zincate (4 wt.% precursor, methanol:oil molar ratio = 12, $T = 60\text{ }^{\circ}\text{C}$).

heterogeneous conditions from different vegetable oils. The resistance to carbonation of the calcium zincate dihydrate could be attributed to its crystallographic structure, formed by chain of tetrahedral Zn^{2+} (4OH^-) sharing corners three-dimensionally linked by isolated octahedral Ca^{2+} (4OH^- and $2\text{H}_2\text{O}$) [33]. In fact, we have compared the as-synthesized precursor and after 100 days in contact with air by EGA-MS and XRD, and the results confirm the stability of the calcium zincate dihydrate against carbonation and hydration.

An important drawback of most solid catalysts used in the transesterification of triglycerides is their low reaction rate in comparison with the homogeneous process. We have compared the catalytic behaviour of a 4 wt.% of precursor, after activation at $400\text{ }^{\circ}\text{C}$ (heterogeneous catalysis) with a methanolic solution containing potassium hydroxide (homogeneous catalysis). It can be seen in Fig. 10 that the FAME yield of activated calcium zincate is very close to values of the homogenous process after 40 min of reaction time, and for longer reaction periods is even higher. The percentage of KOH is low (0.2 wt.%), but if we suppose that the active phase is the CaO, a 4 wt.% of calcium zincate used in the heterogeneous process contains 0.77 wt.% of CaO. The comparison of the homogeneous and heterogeneous processes indicates that basic solid catalysts can reach suitable reaction rate to be used as alternative to conventional base catalysts used in the industrial homogeneous process.

On the other hand, most severe experimental conditions have been used to evaluate the potential of the activate calcium zincate to treat low-grade oils, such as fried oils. For this reason, we have increased the acidity (FFA) of the sunflower oil by adding oleic acid, a typical component of the sunflower oil, as well as evaluated the effect of the water content.

An acid value (mg KOH/g) of 2.18 (equivalent to an acidity degree of 1.1° , defined as g of oleic acid per 100 g of oil) can be found in fried oils [34], whereas the acidity of the refined sunflower oil used in this study is lower than 0.2° . It has been previously demonstrated that, after 1 h of reaction, with edible sunflower oil (0.2° of acidity), a FAME yield close to 100% can be reached. By increasing the acidity until 1.1° , a moderate decreasing of the activity is observed, but the activity is maintained with an acidity value of 0.55° (Table 2). However, the influence of the water content on the FAME yield is more important, since the presence of water provokes a decrease of 20% in the FAME yield after 3 h of reaction. This fact can be explained by taking into account that CaO can be hydroxylated, thus decreasing its activity. The low basicity of hydroxylated phases have been also inferred from the thermal study, since a temperature of $350\text{ }^{\circ}\text{C}$ is not enough to completely dehydroxylate the calcium zincate dihydrate (Fig. 2).

Table 2

Influence of the presence of water and FFA in the sunflower oil on the FAME yield (activation temperature = $400\text{ }^{\circ}\text{C}$, methanol:sunflower oil = 12, $T = 60\text{ }^{\circ}\text{C}$).

Precursor (wt.%)	Time (h)	H_2O (wt.%)	Acidity ($^{\circ}$)	FAME yield (%)
1	3	<0.1	<0.2	100
1	3	0.2	<0.2	79
1	3	1.0	<0.2	61
4	1	<0.1	<0.2	100
4	1	<0.1	0.55	99.7
4	1	<0.1	1.1	88.3

Finally, it is noteworthy that the spent catalyst, after removing by calcination the organic matter deposited during the catalytic runs, is formed by ZnO and CaO which are the raw materials for the synthesis of new calcium zincate dihydrate precursor.

4. Conclusions

Calcium zincate dihydrate is an excellent precursor of a base catalyst for the transesterification of sunflower oil with methanol. The thermal treatment of the precursor at temperatures as low as $400\text{ }^{\circ}\text{C}$ leads to a base catalyst which is very active and stable in biodiesel production from different vegetable oils (sunflower and soybean). The presence of carbonate on the calcium zincate, used as precursor, is negligible after remaining in contact with air for two weeks. The catalyst obtained at $400\text{ }^{\circ}\text{C}$ shows FAME yields higher than 90% after 45 min of reaction time, and the kinetic of the heterogeneous process ($60\text{ }^{\circ}\text{C}$, methanol:oil molar ratio of 12, 4 wt.% of precursor) is very close to that observed under homogeneous conditions (KOH dissolved in methanol). Under these experimental conditions, the catalyst is stable against lixiviation since it can be reutilized for three catalytic runs of 1 h, reaching in each run yields higher than 85%. Moreover, by increasing the acidity of the oil until 1.1° (typical value of fried oils), the catalytic performance is maintained. The presence of water has a negative influence on the catalytic activity, since the addition of a 0.2 wt.% of water into the reaction medium decreases the FAME yield until 80% after 3 h of reaction, although this yield is still higher than 60% after adding a 1 wt.% of water.

Acknowledgements

The authors are grateful to financial support from the Spanish Ministry of Education and Science (ENE2006-15116-C04-02 project) and Junta de Andalucía (PO6-FQM-01661). RMT would like to thanks the Ministry of Science and Innovation (Spain) for the financial support under the Program Ramón y Cajal (RYC-2008-03387).

References

- [1] F. Ma, M.A. Hanna, *Bioresour. Technol.* 70 (1999) 1.
- [2] A. Demirbas, *Energy Convers. Manage.* 50 (2009) 14.
- [3] S. Gryglewicz, *Bioresour. Technol.* 70 (1999) 249.
- [4] H.J. Kim, B.S. Kang, M.J. Kim, Y.M. Park, D.K. Kim, J.S. Lee, K.Y. Lee, *Catal. Today* 93–95 (2004) 315.
- [5] M. Di Serio, M. Ledda, M. Cozzolino, G. Minutillo, R. Tesser, E. Santacesaria, *Ind. Eng. Chem. Res.* 45 (2006) 3009.
- [6] W. Xie, H. Li, *J. Mol. Catal. A* 255 (2006) 1.
- [7] D.G. Cantrell, L.J. Gillie, A.F. Lee, K. Wilson, *Appl. Catal. A* 287 (2005) 183.
- [8] W. Xie, H. Peng, L. Chen, *J. Mol. Catal. A* 246 (2006) 24.
- [9] W. Xie, X. Huang, H. Li, *Bioresour. Technol.* 98 (2007) 936.
- [10] Z. Yang, W. Xie, *Fuel Process. Technol.* 88 (2007) 631.
- [11] M. López-Granados, M.D. Zafra-Poves, D. Martín-Alonso, R. Mariscal, F. Cabello-Galisteo, R. Moreno-Tost, J. Santamaría, J.L.G. Fierro, *Appl. Catal. B* 73 (2007) 317.
- [12] M.C.G. Albuquerque, I. Jiménez-Urbistondo, J. Santamaría-González, J.M. Mérida-Robles, R. Moreno-Tost, E. Rodríguez-Castellón, A. Jiménez-López, D.C.S. Azevedo, C.L. Cavalcante Jr., P. Maireles-Torres, *Appl. Catal. A* 334 (2008) 35.
- [13] E. Lotero, Y. Liu, D.E. Lopez, K. Suwannakarn, D.A. Bruce, J.G. Godwin Jr., *Ind. Eng. Chem. Res.* 44 (2005) 5353.

- [14] M. Di Serio, M. Cozzolino, R. Tesser, P. Patrono, F. Pinzari, B. Bonelli, E. Santacesaria, *Appl. Catal. A* 320 (2007) 1.
- [15] S. Furuta, H. Matsuhashi, K. Arata, *Catal. Commun.* 5 (2004) 721.
- [16] H. Fukuda, A. Kondo, H. Noda, J. Biosci. Bioeng. 92 (2001) 405.
- [17] M.K. Modi, J.R.C. Reddy, B.V.S.K. Rao, R.B.N. Prasad, *Bioresour. Technol.* 98 (2007) 1260.
- [18] G. Madras, C. Kolluru, R. Kumar, *Fuel* 83 (2004) 2029.
- [19] A. Demirbas, *Bioresour. Technol.* 99 (2008) 1125.
- [20] H. Zhu, Z. Zongbin, Y. Chen, P. Zhang, S. Duan, X. Xiaohua, Z. Mao, *Chin. J. Catal.* 27 (2006) 391.
- [21] C.R.V. Reddy, R. Oshel, J.G. Verkade, *Energy Fuels* 20 (2006) 1310.
- [22] G. Arliguie, J. Grandet, *J. Cem. Concr. Res.* 20 (1990) 517.
- [23] J. McBreen, *J. Electrochem. Soc.* 111 (1972) 1620.
- [24] F. Liebau, A. Amel-Zadeh, *Kristall Technik* 7 (1972) 221.
- [25] S. Wang, Z. Yang, L. Zeng, *Mater. Chem. Phys.* 112 (2008) 603.
- [26] F. Ziegler, C.A. Johnson, *Cem. Concr. Res.* 31 (2001) 1327.
- [27] J.C. Dupin, D. Gonbeau, P. Vinatier, A. Levasseur, *Phys. Chem. Chem. Phys.* 2 (2000) 1319.
- [28] M. Kouzu, T. Kasuno, M. Tajika, S. Yamanaka, J. Hidaka, *Appl. Catal. A* 334 (2008) 357.
- [29] C. Ngamcharussrivichai, P. Totarat, K. Bunyakiat, *Appl. Catal. A* 341 (2008) 77.
- [30] A.H. Delgado, R.M. Paroli, J.J. Beaudoin, *Appl. Spectrosc.* 50 (1996) 970.
- [31] T.C. Lin, M.Y.A. Mollah, R.K. Vempati, D.L. Cocke, *Chem. Mater.* 7 (1995) 1974.
- [32] H. Zhu, Z. Wu, Y. Chen, P. Zhang, S. Duan, X. Liu, Z. Mao, *Chin. J. Catal.* 27 (2006) 391.
- [33] R. Stahl, H. Jacobs, *Z. Anorg. Allg. Chem.* 623 (1997) 1287.
- [34] G. Bansal, W. Zhou, T.-W. Tan, F.-L. Neo, H.-L. Lo, *Food Chem.* 116 (2009) 535.